

EVALUATION OF CHITOSAN ELECTRODEPOSITED ON SS-316 AND EXPOSED TO A CHLORIDES SIMULATED BODY FLUID

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Abstract: The effect of the molecular weight of coatings of electro-deposited chitosan on a SS-316 was studied, using electrophoresis and then the anticorrosive resistance was evaluated, by means of electrochemical methods like linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) in a chlorides solution of NaCl (0.5M) simulating a human body fluid. The results show a better behavior of the chitosan of high and low molecular weight and the reinforcement of the mechanical properties of the biopolymer when using the reagent glutaraldehyde. Also is included the electrochemical characterization of chitosan membranes with Infrared (IRS) and Raman (RS) spectroscopy, as well as surface morphology with scanning electron microscopy (SEM) and elemental analysis by X-ray dispersion (EDS).

KEYWORDS: Chitosan, Biopolymer, Electrodeposition, Simulated body fluid, Stainless steel.

INTRODUCTION

The field of biomaterials has been addressed in recent years towards biomedical applications and specifically in the human body, due to the diversity of problems that occur in vital organs such as the heart, skin, joints, but especially in prostheses for implants in regeneration of fractured bones [Abraham et al, (1998), Bang et al, (2006), Croisier & Jérôme, (2013), Gil et al, (2003), Huebsch & Mooney, (2009), Park & Lakes, (2007) and Ratner et al, (1990)]. The development of innovative non-metallic biomaterials is a search of great scientific interest, the evolution of biomaterials in the last 50 years has been spectacular. It has gone from using inert materials for the replacement of living tissues, to the design of bioactive and biodegradable materials for their repair, which has led to the third generation of biomaterials, where the goal is already to regenerate [(Gil

etal, (2003), Park & Lakes, (2007) and Ratner et al, (1990)].

Since the middle of the last century industrial materials have been used for medical applications, the only thing that was taken care of is that it had no reaction when in contact with body fluids without taking into account its biocompatibility. The importance of polymers as biomaterials is reflected in the size of the polymer market for medical uses, which is estimated at about US \$ 1 billion. Natural polymers such as chitosan, in recent years has been of great interest due to the properties it presents, such as its biocompatibility, which basically is the ability of a material to be accepted by the human body, that is, it does not cause irritation with the surrounding tissues, do not cause inflammation or a carcinogenic reaction [Croisier & Jérôme, (2013), Kumara & Buchheita ,(2006) and Black, (2006)].

The use of biopolymers as coatings has the purpose of slowing down the corrosion rate in metals. In this case, the interest is to observe the anticorrosive behavior of the chitosan biopolymer used as a coating. The combination of both metal and polymer biomaterials, seeks to control the rate of biodegradation by corrosion of said material and also that the biopolymer is able to provide antibacterial immunity by containing bactericidal substances that prevent infection and poisoning by corrosion products from the substrate metallic in contact with biological fluids, considering the characteristics of biocompatibility and biodegradability [Alzate et al, (2015), Andrade & Feliu, (1991), Ávila & Genescá (1996), López et al, (2004), Mina et al, (2013), Ramírez & Uruchurtu, (2007)].

The coating has been obtained by the electrophoresis technique in voltage ranges from 8 to 12 V with the help of a supporting electrolyte of KCl and a 2-electrode array, using a platinum counter electrode and a

working electrode of SS- 316. The membranes of chitosan of several molecular weight are shown in the figure 1, although a considerable thickness of the biopolymer was also detected, the presence of porosity was observed, which does not allow to obtain a considerable homogeneity [Vázquez, (2007), Artavia, (2008), Cerón et al, (2010)].

EXPERIMENTAL WORK

ELECTRODEPOSITION OF CHITOSAN COATINGS

PREPARATION OF CHITOSAN SOLUTION

The chitosan solutions with several molecular weights were prepared at 1 and 2% of polymer in reactive grade citric acid, the chitosan solution was made at a temperature of 60°C and the solutions were stirred at 6 rpm until total dissolution. They were allowed to cool 24 hrs before being used.

ELECTRODEPOSITION

For the configuration of the electrochemical cell the arrange of two electrodes was used (against graphite electrode and the working electrode the SS-316), immersed in a solution of chitosan and also using a supporting electrolyte of KCl 1M, for better conductivity of the medium and facilitate the formation of the chitosan coating by means of the electrophoresis method. With a power source mark GW model GPR-3510HD, a voltage of 9.1 V was applied and was maintained for a time of two minutes, the coatings obtained were dried with a hot air jet for 2 minutes to avoid over drying of the membranes. Once obtained the membranes were wetted with a drop of Glutaraldehyde reactive grade solution and stored in silica gel desiccator conditions until the electrochemical testing become.

ELECTROCHEMICAL EVALUATION

The measurements were made with a volume of 250 ml of the chlorides solution of NaCl (3.5% by weight), forming the electrochemical cell with a 3-electrode array, using a reference electrode of Ag/AgCl, a counter electrode of graphite and the working electrode with the specimen of SS-316 and coated with chitosan. For the electrochemical monitoring a Potentiostat-Galvanostat model PocketStat brand Ivium was used and the applied electrochemical techniques were the linear polarization resistance (LPR) in a range of ± 15 mV with a sweep of 1 mV/s and the electrochemical impedance spectroscopy (EIS) by applying a sinusoidal ac voltage signal 10 mV and performing a sweep in the frequency domain in a range of 10^4 to 10^{-2} Hertz. The electrochemical evaluation was monitored at 0, 6 and 24 hr respectively.

PHYSICOCHEMICAL CHARACTERIZATION OF CHITOSAN

For the physicochemical characterization of electrodeposited chitosan coatings, before and after their electrochemical evaluation, different techniques were used, such as Raman and Infrared spectroscopy, as well as Scanning electron microscopy (SEM). With the Raman diagrams, information is sought on the molecular composition of the sample, whose dispersion is produced by the variation of frequencies different from that of the incident radiation, where the frequency variations are associated with energy variations and being a technique that offers versatile advantages, since it allows to analyze any sample without depending on the state in which it is found: gases, liquids, films, powders, pastes among others [Mendoza et al, (2006)]. The Infrared spectroscopy consists in the influence with

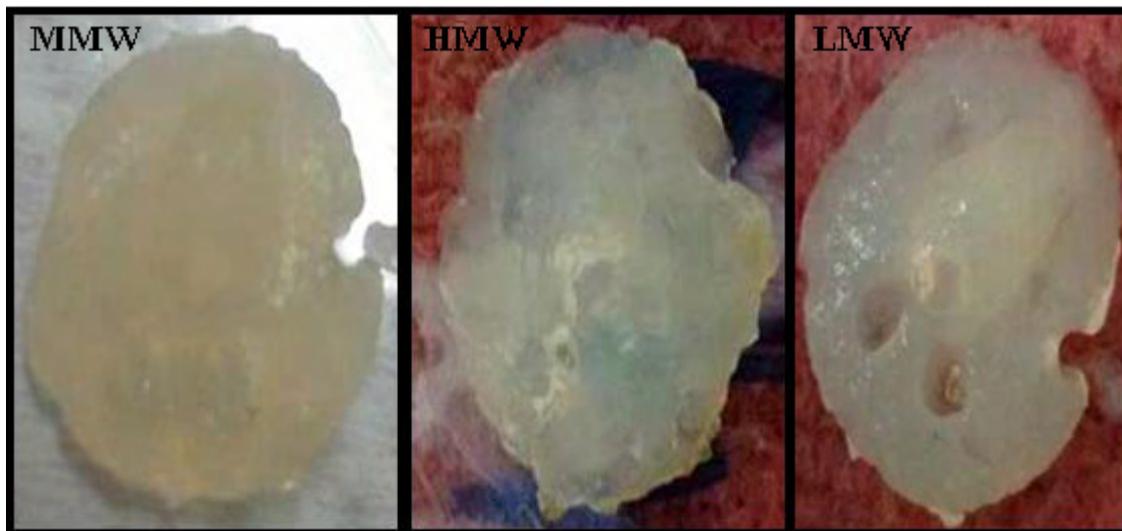


Figure 1. Electrodeposited membranes of chitosan as medium, high and low molecular weight.

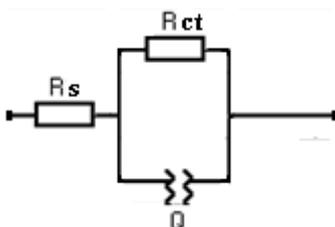


Figure 2. Equivalent circuit applied to the electrochemical impedance data.

Time, Hr	RS	Alpha	Q	Rtc	C	CR, mm/ year	T= R _{ct} *C _{dl}
Bare SS-316							
0	11,06	0,858	4,57E-05	2,35E+05	9,79E-05	3,62E-03	2,30E+01
6	11,5	0,884	4,40E-05	3,62E+05	8,76E-05	2,46E-02	3,17E+01
24	11,67	0,87	3,96E-05	4,52E+06	7,91E-05	3,07E-02	3,58E+02
HMW+ Glutaraldehyde							
0	24,2	0,69	7,25E-05	2,66E+05	9,43E-05	2,63E-02	2,51E+01
24	20	0,77	5,60E-05	5,47E+05	7,57E-05	3,52E-02	4,14E+01
LMW+ Glutaraldehyde							
0	11	0,7	6,90E-05	3,19E+05	1,93E-04	3,67E-01	6,17E+01
6	13	0,8	3,45E-05	2,00E+06	6,84E-05	3,54E-02	1,37E+02
24	15	0,82	3,02E-05	1,00E+07	5,04E-05	8,13E-03	5,04E+02

Table I. Electrochemical parameters of applying the equivalent circuit to the chitosan membranes electrodeposited+ Glutaraldehyde on SS-316 and exposed in the chlorides solution.

infrared radiation, and from there it is determined how much radiation was absorbed in some energy in particular and that it can belong to a specific functional group, so the appearance of a peak in a corresponding energy to the frequency in which occur the vibration of a specific molecule [Medina et al, (2003)]. The SEM technique consists of the use of a microscope which generates an image and physical-chemical data of the surface using a thin electron beam which scans the surface of the specimen that is inside a vacuum chamber and with the help of the detectors can obtain the information emanating signals provided by the electron beam [Stuart, (2004)]. In addition, this technique allows obtaining a better resolution of digital images compared to an optical microscope and elemental chemical analysis in micrometric zones by X-ray dispersion, or with the mapping for each element of interest selectively, its main application is in the obtaining topographic images in magnitudes of 10-1000 nm range.

RESULTS AND DISCUSSION

For the analysis of the impedance response in each of the membranes, an equivalent circuit model shown in Fig. 2 was applied to the results, which explains the phenomena that are occurring in the electrolyte-membrane-metal interface [MacDonald, (1984)]. The electrical parameters that have been obtained are shown in table I.

For the calculation of capacitances, the equation 1 known as the Brug's expression [Brug et al, (1984)], was used, where the electrolyte resistance (R_s) and the charge transfer resistance (R_{ct}) are related, which allow obtaining the capacitance based on the parameter Q known as a constant phase element (CPE) which is an empirical representation of the admittance (Y_o) expressed as $Q = Y_o (j\omega)^{-\alpha}$, where the coefficient (α) is related to the amplitude of the distribution of the relaxation

times in a range of $-1 \leq \alpha \leq 1$.

$$C = Q^{1/\alpha} \left(\frac{1}{R_e} + \frac{1}{R_{ct}} \right)^{\frac{1-\alpha}{-\alpha}} \quad [1]$$

Figure 3 shows the results of the corrosivity of the SS-316 systems with and without the electro deposited Chitosan and with the effect of the molecular weight as the commercial grade chitosan was acquired.

The Fig. 3(a) is showing the double layer capacitance and charge transfer resistance behavior for the several molecular weight of chitosan, observing how the Cdl in the HMW was highly and nearly constant than the LMW which was behave lowing in the first 6 hr and then nearly constant. The Rct behavior was observed lower and nearly constant in the HMW, while the LMW was higher and increasing in the first 6 hr. The corrosion rate of Fig. 3(b) was determined by LPR method and observed how them follows the capacitance tendency, as the HMW was lower in the first 6 hr and then nearly constant than the LMW that is higher in the beginning, but with quick lowering in the first 6 hr and then behave with a nearly constant lowering with the immersion time, including comparison with the bare SS-316. Also, was observed the behavior of the time constant $T = R_{ct} * C_{dl}$, which follows the Rct tendency in the coated systems. So, it was observed a slight advantage in the anticorrosive resistance provided by the chitosan LMW, accord with the similar behavior observed in the capacitance and corrosiveness response [Scully, (1986)], indicating that the porosity area could be increasing and leaving space to the SS-316 for the passive layer formation. As in the HMW the capacitance does not change, that's can be the consequence for high corrosiveness registered and probably attributed to a less adhesively between the electro coated chitosan and the metal surface [(McIntyre and Leidheiser, (1985)]. Figures 4(a) and 4(b) show the diagrams of Nyquist

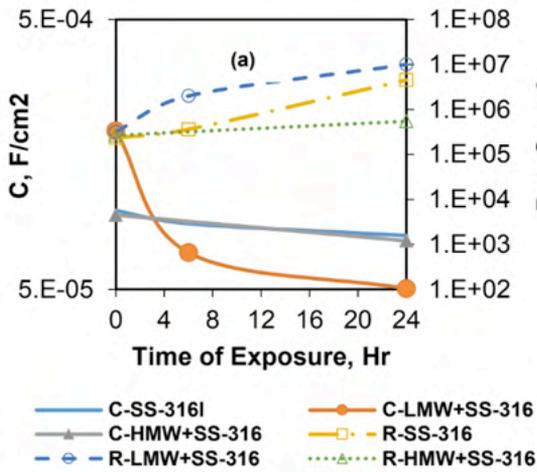


Figure 3(a). C_{dl} and R_{ct} over bare SS316 with electrodeposited chitosan+ Glutaraldehyde with two molecular weight.

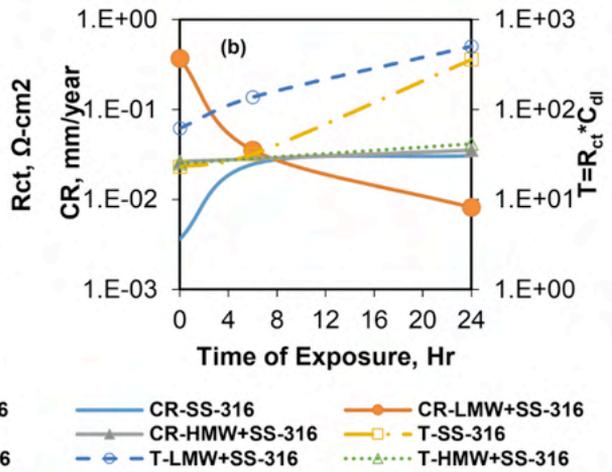


Figure 3(b). Corrosiveness and Time Constant of the membranes of chitosan+ Glutaraldehyde In function of the molecular weight.

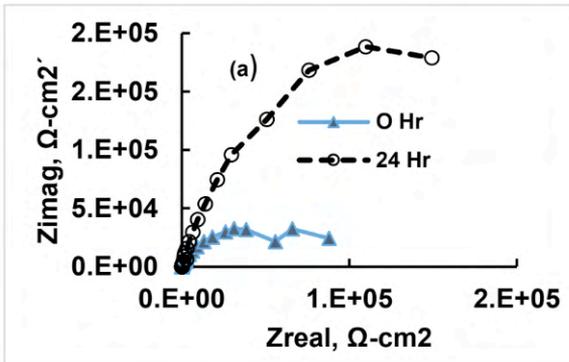


Figure 4(a). Nyquist diagrams of the LMW.

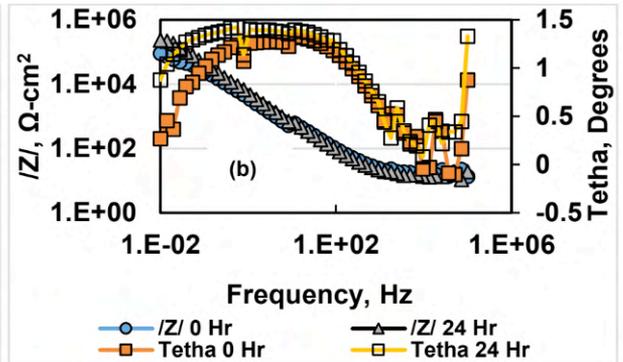


Figure 4(b). Bode diagrams of the LMW.

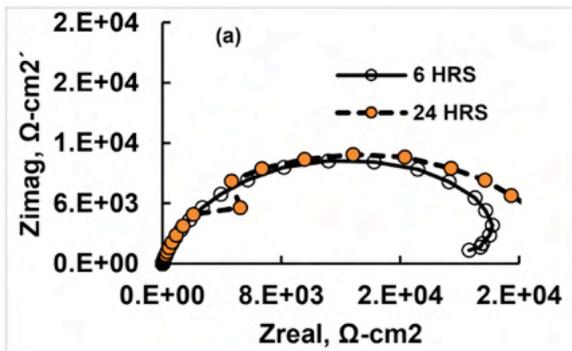


Figure 5(a). Nyquist diagrams of the HMW.

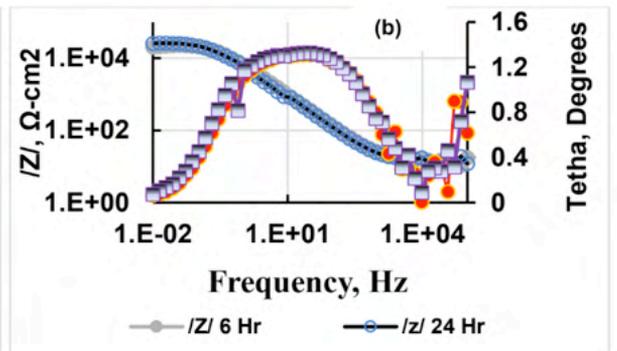


Figure 5(b). Bode diagrams of the HMW.

and Bode representing the behavior of the chitosan LMW coatings exposed for 24 h in the chlorides solution. Figures 5(a) and 5(b) show the process that had the HMW coating against a chlorides solution, attributing its behavior to the molecular weight, the polymer chains tend to be larger and hinder its degradation.

In the Nyquist diagrams a tendency of the SS-316 with the Bio-polymer system to increase its resistance with the exposure time is observed, while in the LMW it increases from 1.25×10^3 to $3 \times 10^5 \Omega \cdot \text{cm}^2$ and the HMW increases only slightly from 2.5×10^4 to $2.8 \times 10^4 \Omega \cdot \text{cm}^2$. However, in the Bode diagrams in the impedance module $|Z|$, it is only possible to observe a time constant clearly, but in the phase angle θ , it can be observed that there is information in the high frequency only indicating the presence of a time constant attributable to the coating film and retains some integrity better in LMW than the HMW coatings. Also, when observing the low frequency range, the LMW coating shows changes attributable to a higher resistance of limited diffusion which it could be interpreted as a better behavior impervious to the passage of ionic substances through the membrane, which is not observed in the coating of HMW to show lower diffusion resistance and that is interpreted as more permeable to the passage of ions and then less protection of the SS substrate.

The Infrared spectra are shown in Figures 6(a) and 6(b) for the chitosan LMW, in reactive grade and in the electrodeposited membrane, in Figures 7(a) and 7(b) the respective spectra are shown for the chitosan HMW in reactive grade and as a membrane respectively, showing that there are no significant differences in the functional groups attributable to the molecular weight.

The Raman diagrams of the figures 8(a) and 9(a), show differences in the intensity since

the LMW it starts near of 3000 cm^{-1} , while the HMW does it near the 260, semi-stabilizing itself from the 500 cm^{-1} , such behavior may be due to the viscoelastic properties of the polymer since there is a better accommodation of the polymer chains in the chitosan LMW that has greater flexibility compared to the chitosan HMW where the crystallinity of the polymer chains produces greater rigidity. This behavior can also be related to the degree of de-acetylation, since the LMW contains up to 70%, while the HMW is very close to 90% de-acetylation [Alzate et al, (2015)]. Figures 8(b) and 9(b) show the IR light passing through the membranes surface, which is highly for the LMW than the HMW attributable to the porosity degree of the produced membranes.

The SEM microscopy in the morphological surface is shown in Figures 10(a) and 11(a) and its respective chemical composition by EDX is shown in Figures 10(b) and 11(b), for the LMW and the HMW respectively. As observed in both membranes the main component is KCl, especially in the LMW, while in the HMW a greater number of elements is detected, which may be due to the high undercoated corrosiveness and as the membrane was less porous retaining the metal ions coming from of the metallic substrate of SS-316.

CONCLUSIONS

1. Chitosan of different molecular weights in solution can be electro-deposited successfully on substrates of SS-316 applying the electrophoresis method.
2. The electrodeposited chitosan membranes showed a variable behavior in the anticorrosive protection resistance to the metallic substrate, attributable to the mechanical properties that influences the porosity degree formed during the electrophoresis process.

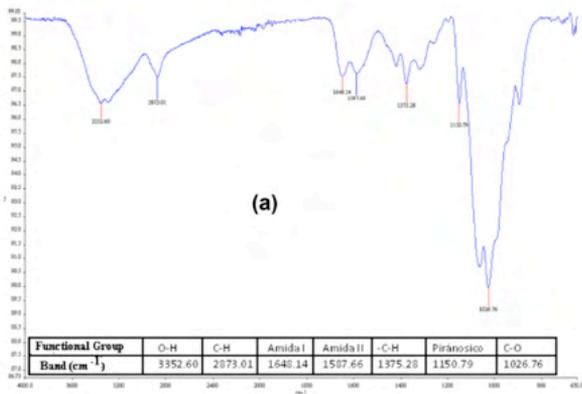


Figure 6(a). Infrared spectra of chitosan LMW reactive degree.

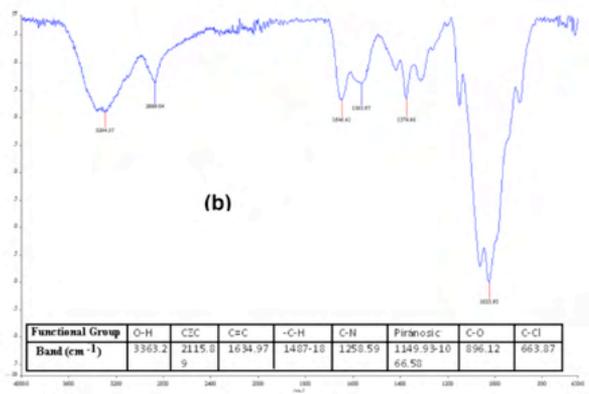


Figure 6(b). Infrared spectra of chitosan HMW reactive degree.

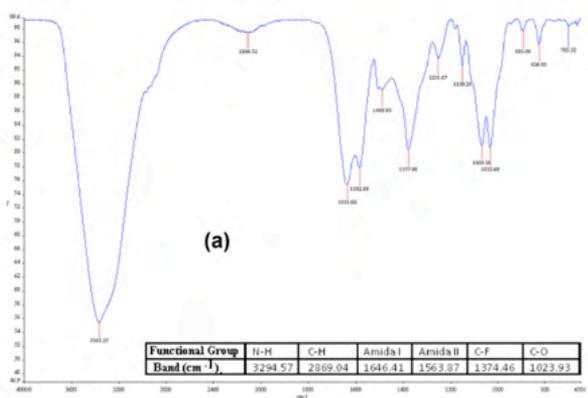


Figure 7(a). Infrared spectra of chitosan LMW electrodeposited.

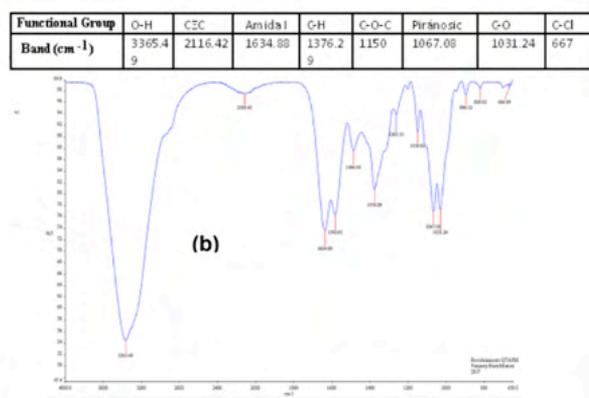


Figure 7(b). Infrared spectra of chitosan HMW electrodeposited.

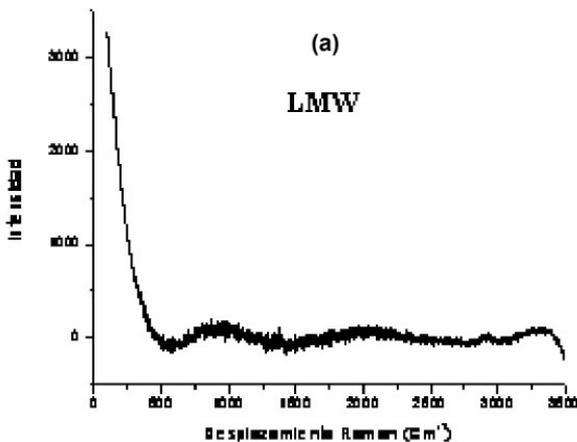


Figure 8(a). Raman spectra of chitosan LMW electrodeposited.

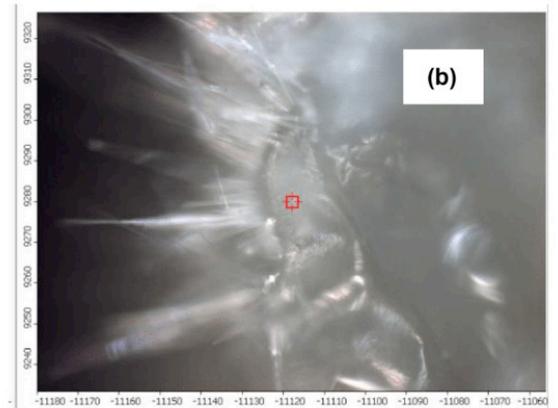


Figure 8(b). Photo of the Raman zone analyzed on chitosan LMW electrodeposited.

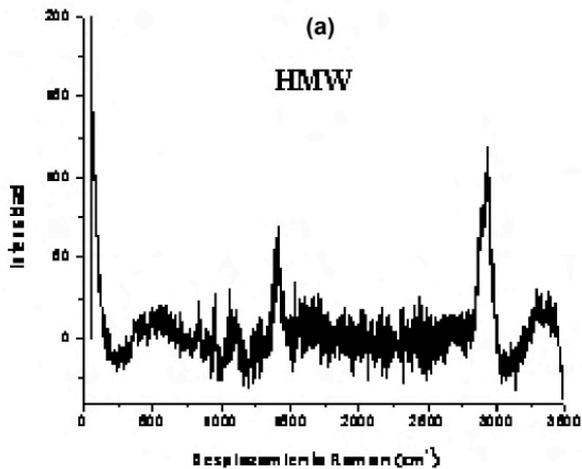


Figure 9(a). Raman spectra of chitosan HMW electrodeposited.

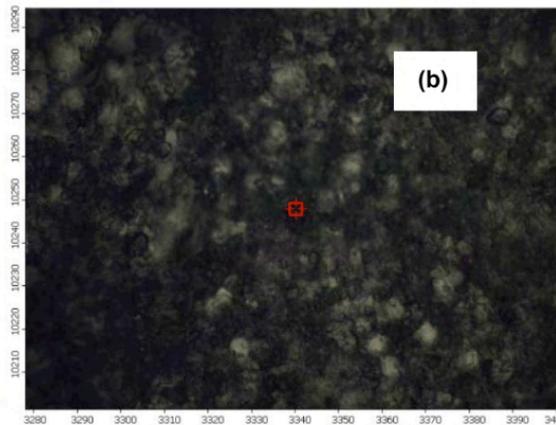


Figure 9(b). Photo of the zone analyzed of chitosan HMW electrodeposited.



Figure 10 (a). Photomicrography of electrodeposited LMW.

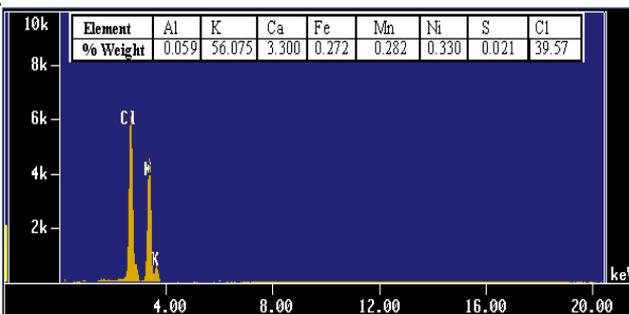


Figure 10(b). Elemental Chemical analysis of chitosan LMW

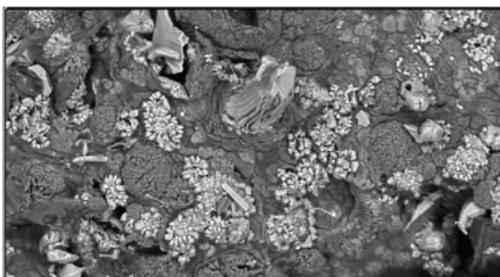


Figure 11 (a). Photomicrography of HMW electrodeposited.

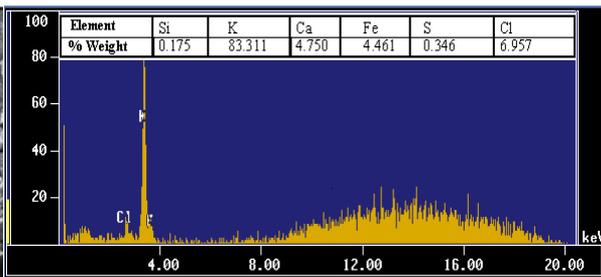


Figure 11(b). Elemental Chemical analysis of chitosan HMW.

3. The LMW chitosan membrane showed greater porosity and better resistance to degradation in the electrochemical evaluation, probably because it allows the passivation of the SS-316 to occur due to less ionic restriction, while the HMW, being less porous, does not allow complete the re-passivation film and in areas with braked passive layer the corrosion process was increased as demonstrated in the electrochemical response of LPR and EIS.

4. The membranes of the biopolymer of chitosan are very difficult to study in their surface morphology with SEM

and only chemical composition with Raman spectroscopy it was possible to relate the level of crystallinity and the molecular weight of the polymer chains with the degree of de-acetylation and how this behavior can be reflected in its rheological and viscoelastic properties, which also could be connected with the anticorrosive behavior over metallic substrates.

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